Chemoselectivity of the [2+3]-Cycloaddition of Thiocarbonyl Ylides with 5-Benzylidene-3-phenylrhodanine

Seyfried, M S ; Linden, Anthony ; Mlostoń, Grzegorz ; Heimgartner, H

Abstract: Reactions of three different thiocarbonyl S-methylides, generated from thiobenzophenone (2), 2,2,4,4-tetramethyl-3-thioxocyclobutanone (3), and adamantanethione (8), respectively, and diazomethane, with 5-benzylidene-3-phenylrhodanine (12) were carried out. The aromatic thiocarbonyl ylide 1a adds chemoselectively to the C,C-double bond, but the spirocyclic 1,3-dithiolane 18, i.e. the [2+3]-cycloadduct with the C=S group of 12,was also formed as a minor product. In the cases of the aliphatic thiocarbonyl ylides 6 and 20, the [2+3]-cycloaddition occurred at the exocyclic C,C-double bond exclusively to give the spirocyclic tetrahydrothiophene derivatives 23 and 21, respectively. A smooth acid-catalyzed decomposition of 18 yielded the 2-diphenylmethylidene derivative 19. The formation of product 24, which was obtained in the reaction of the sterically congested ylide 6 with 12, is explained by a 1,4-H-shift in an intermediate zwitterionic adduct. The structures of the tetrahydrothiophenes 17, 21 and 23, as well as that of 24, were established by X-ray crystallography.

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Chemoselectivity of the [2+3]-Cycloaddition of Thiocarbonyl Ylides with 5-Benzylidene-3-phenylrhodanine

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Reactions of three different thiocarbonyl *S*-methylides, generated from thiobenzophenone (**2**), 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**3**), and adamantanethione (**8**), respectively, and diazomethane, with 5-benzylidene-3-phenylrhodanine (**12**) were carried out. The aromatic thiocarbonyl ylide **1a** adds chemoselectively to the C,C-double bond, but the spirocyclic 1,3-dithiolane **18**, *i.e*. the [2+3]-cycloadduct with the C=S group of **12**, was also formed as a minor product. In the cases of the aliphatic thiocarbonyl ylides **6** and **20**, the [2+3]-cycloaddition occurred at the exocyclic C,C-double bond exclusively to give the spirocyclic tetrahydrothiophene derivatives **23** and **21**, respectively. A smooth acid-catalyzed decomposition of **18** yielded the 2-diphenylmethylidene derivative **19**. The formation of product **24**, which was obtained in the reaction of the sterically congested ylide **6** with **12**, is explained by a 1,4-H-shift in an intermediate zwitterionic adduct. The structures of the tetrahydrothiophenes **17**, **21** and **23**, as well as that of **24**, were established by X-ray crystallography.

Key words: thiocarbonyl ylides, 1,3-dipolar cycloaddition, rhodanine, 2,5-dihydro-1,3,4-thiadiazoles, crystal structure

Although the fruitful concept of 1,3-dipolar cycloaddition was formulated by Huisgen as early as 1963 [1] (see also [2,3]), and some [2+3] cycloadditions with thioketones were observed early in the last century [4,5],*** the usefulness of the C=S group as a dipolarophile was recognized only in the 1980s [6,7]. Since then, a large series of [2+3] cycloadditions with C=S compounds have been investigated and their reaction mechanisms established. As a result of kinetic studies, thioketones are now recognized as extraordinarily reactive dipolarophiles and are called 'superdipolarophiles' [8–11].

In the last few years, interest in thiocarbonyl ylides as 1,3-dipoles has increased [12,13]. Their reaction with C=S containing compounds, such as aromatic and cycloaliphatic thioketones [14–16], dithioesters [15,16], trithiocarbonates [15], and 1,3-thiazole-5(4*H*)-thiones [17], leads to 1,3-dithiolanes ('Schönberg reaction' [14,18],

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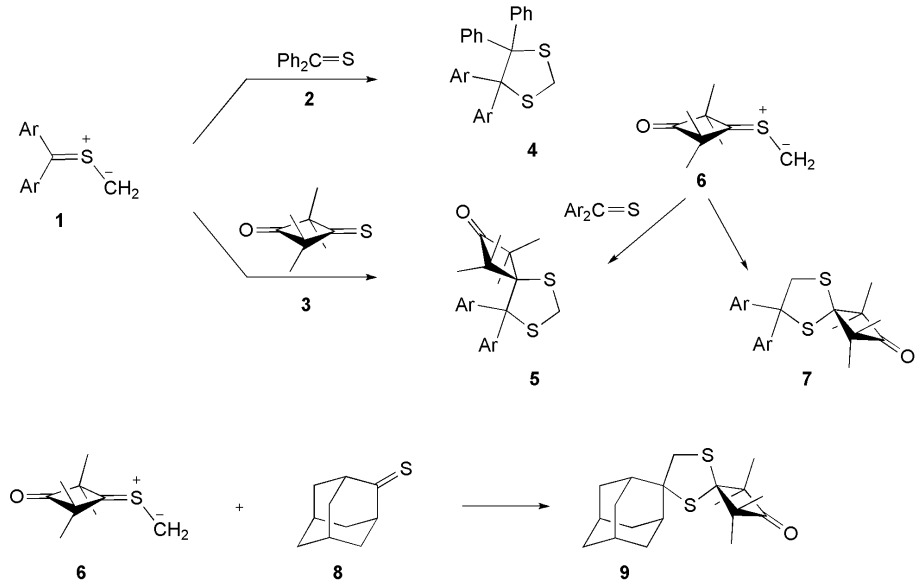
*** At that time, the mechanism of the formation of the described products was unknown.

Scheme 1). Aromatic thioketone *S*-methylides **1** react with aromatic as well as cycloaliphatic thioketones (*e.g.* **2** and **3**) to give the sterically crowded 1,3-dithiolanes of type **4** and **5**, respectively, in a regioselective manner [14,15,19]. On the other hand, the reactions of cycloaliphatic thioketone *S*-methylides, such as **6** with **2**, lead to mixtures of 1,3-dithiolanes, *e.g.* **5** and **7** in favor of the sterically congested **5** [16,18,20]. Finally, the sterically less crowded products of type **9** are formed regioselectively in reactions of cycloaliphatic thioketone *S*-methylides with aliphatic thioketones (*e.g.* **6** and **8**) [16,18,20].

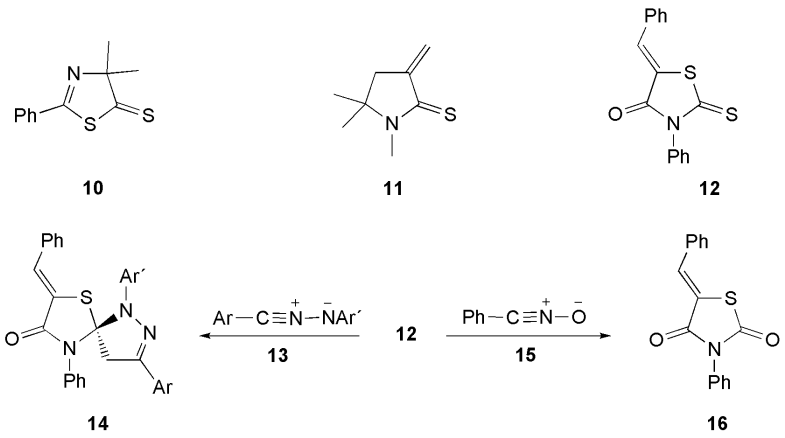
Scheme 1



In addition to thioketones, heterocyclic thiones **10**–**12** (Scheme 2) have been used as C=S dipolarophiles. For example, benzonitrile oxides, imides and ylides [21], diazo compounds [22], azomethine ylides [23], carbonyl ylides [24] and thiocarbonyl ylides [17] react exclusively with the C=S group of **10**. On the other hand, benzonitrile oxide (**15**) and nitrones add chemoselectively to the C,C-bond of **11** [25], whereas reactions of benzonitrile imides **13** and benzonitrile oxide (**15**) with the rhodanine derivative **12** yield cycloadducts **14** [26] and 1,3-thiazolidine-2,4-dione **16**, respectively. In the latter case, the initially formed cycloadduct, a spirocyclic 1,4,2-oxathiazole derivative, is not stable and a subsequent cycloreversion leads to the final product [27].

Recently, we investigated further 1,3-dipolar cycloadditions with **12**, which contains three different π-systems as potential dipolarophilic groups. In the present paper, new results of the reactions of **12** with thiocarbonyl *S*-methylides **1a**, **6** and **20** are discussed.

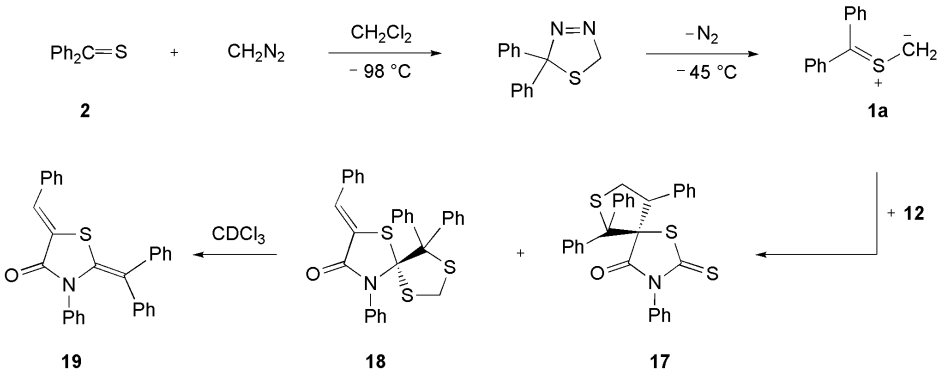
Scheme 2



RESULTS AND DISCUSSION

According to the protocol in [15], thiobenzophenone *S*-methylide (**1a**) was generated *in situ* in dichloromethane at low temperature in the presence of the rhodanine derivative **12** [28]. After stirring overnight at room temperature, chromatographic workup gave two 1:1 adducts **17** and **18**, which were isolated in 61 and 3% yield, respectively (Scheme 3). Furthermore, 30% of the starting material **12** was recovered. The ESI-MS of the two adducts showed that they are isomers (m/z = 532 (100, $[M + Na]^+$)), and the ^{13}C-NMR spectra revealed the presence of a C=S group in **17** (198.9 ppm) and the absence of this group in **18**. As in both cases a carbonyl group was detected (IR, ^{13}C-NMR), **17** is the C=C adduct and **18** the expected C=S adduct. The structure of **17** was established by an X-ray crystal structure analysis (Figure 1).

Scheme 3



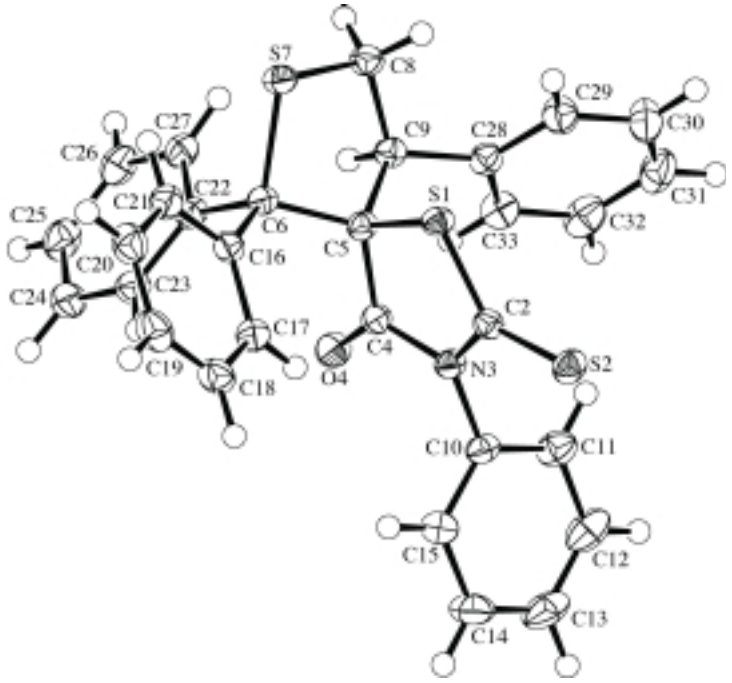


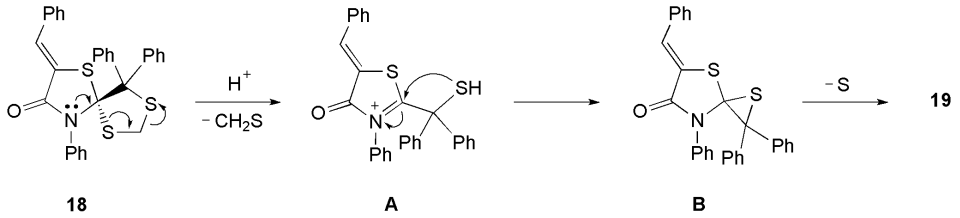
Figure 1. ORTEP-plot [29] of the molecular structure of **17** (arbitrary numbering of the atoms; 50% probability ellipsoids).

In the case of **18**, the structure was assigned on the basis of the spectroscopic data. The regioselectivity of the cycloaddition, *i.e*. the formation of the more crowded 1,3-dithiolane, follows from the NMR absorption of the CH_2 group (*AB* at 3.84 and 3.59 ppm, $J = 8.4$ Hz, *t* at 31.9 ppm; see [15,18]). Under slightly acidic conditions in $CDCl_3$, **18** decomposed to give the known product **19*** in quantitative yield. The structure of product **19** proves the presence of a C,C bond between Ph_2C and C(2) of the 1,3-thiazolidine ring in **18**. A reaction mechanism for the decomposition of **18** is proposed in Scheme 4 (see also [31]). Elimination of thioformaldehyde under acid catalysis could lead to intermediate **A**, which forms the spirocyclic thiirane **B** *via* nucleophilic attack of the thiole group at the iminium C-atom. Subsequently, elimination of sulfur from **B** yields the isolated product **19**. The last reaction is also responsible for the formation of **19** in the reaction of **12** with diphenyldiazomethane [30].

Similarly, the reaction of **12** with adamantanethione *S*-methylide (**20**) was carried out: diazomethane was added to a solution of admanatanethione (**8**) in toluene at –20°C and, after decolorization of the solution, **12** was added and the mixture

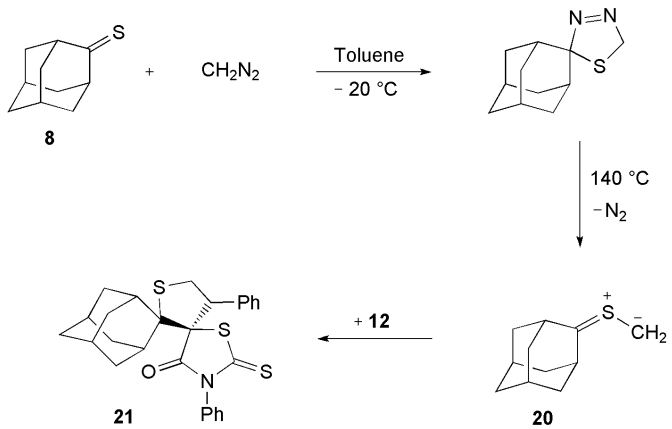
*Compound **19** has been prepared independently of **12** and diphenyldiazomethane in refluxing toluene [30].

Scheme 4



refluxed for 12 h. Chromatographic workup gave 28% of the 1:1-cycloadduct **21** and 29% of the starting material **12** (Scheme 5). No additional product could be detected. The relatively low yield of **21** can be explained by the fact that the treatment of **8** with diazomethane leads to a mixture of the 1,3,4-thiadiazole (the precursor of **20**) and the 1,2,3-isomer [16]. The latter does not eliminate N_2 to give **20** on heating but decomposes during chromatographic workup. The structure of **21** was established by X-ray crystallography (Figure 2). These results show that the 1,3-dipolar cycloaddition of **20** with **12** occurred exclusively at the C,C-double bond, and not at the thiocarbonyl group. Furthermore, it is worth mentioning that the sterically less favored cycloadduct is formed.

Scheme 5



Finally, the reaction of 2,2,4,4-tetramethyl-3-oxocyclobutanethione *S*-methylide (**6**) with **12** was performed. The precursor of **6**, the 2,5-dihydro-1,3,4-thiadiazole **22**, was prepared from 2,2,4,4-tetramethyl-3-thioxobutanone (**3**) and diazomethane in diethyl ether at –78°C and crystallized from pentane [20]. A solution of **12** and 1.4 equivalent of **22** in THF was heated to 50°C. The nitrogen evolution ceased after 2 h. Then, the solvent was evaporated and the residue separated by means of column chromatography. In addition to 74% of the starting material **12**, two isomeric products

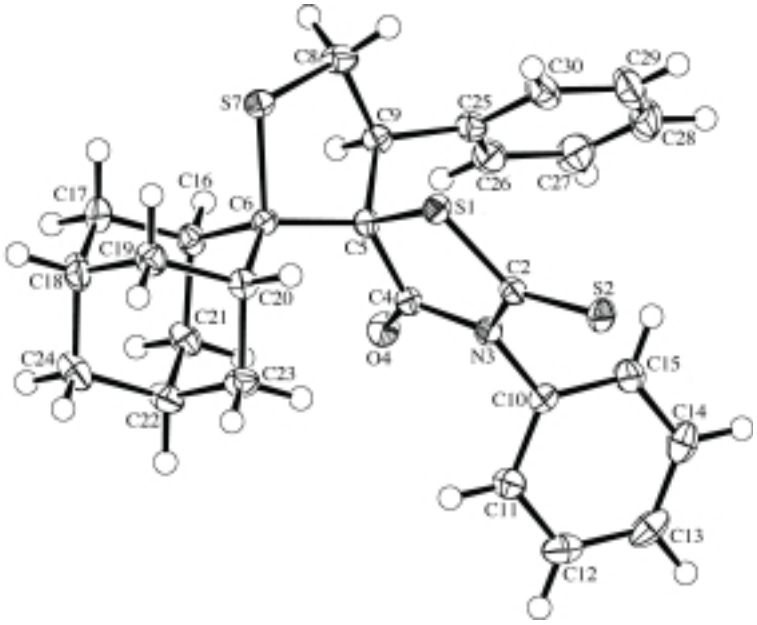
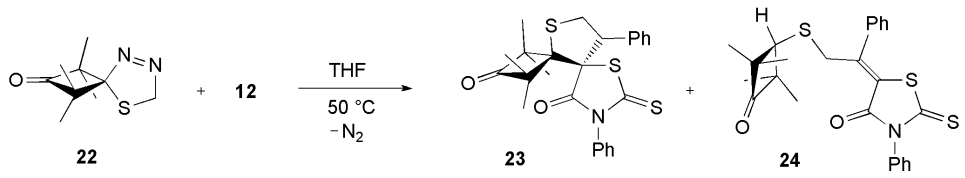


Figure 2. ORTEP-plot [29] of the molecular structure of **21** (arbitrary numbering of the atoms; 50% probability ellipsoids).

with the molecular weight of 1:1-adducts (ESI-MS: m/z = 490 (100, $[M + Na]^+$)) were obtained in **8** and 10% yield, respectively*. Based on the spectroscopic data, the first product was assigned the structure of the cycloadduct **23** (Scheme 6). The regioselectivity of the cycloaddition was indicated by the similarity of the NMR absorptions of the $–CH_2–CHPh–$ fragment in adducts **17**, **21** and **23**. Finally, the structure of **23** was established by X-ray crystallography (Figure 3).

Scheme 6



* In the crude reaction mixture, significant amounts of 4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexan-5-one [32], the product of the 1,3-dipolar electrocyclization of the thiocarbonyl ylide **6**, were detected.

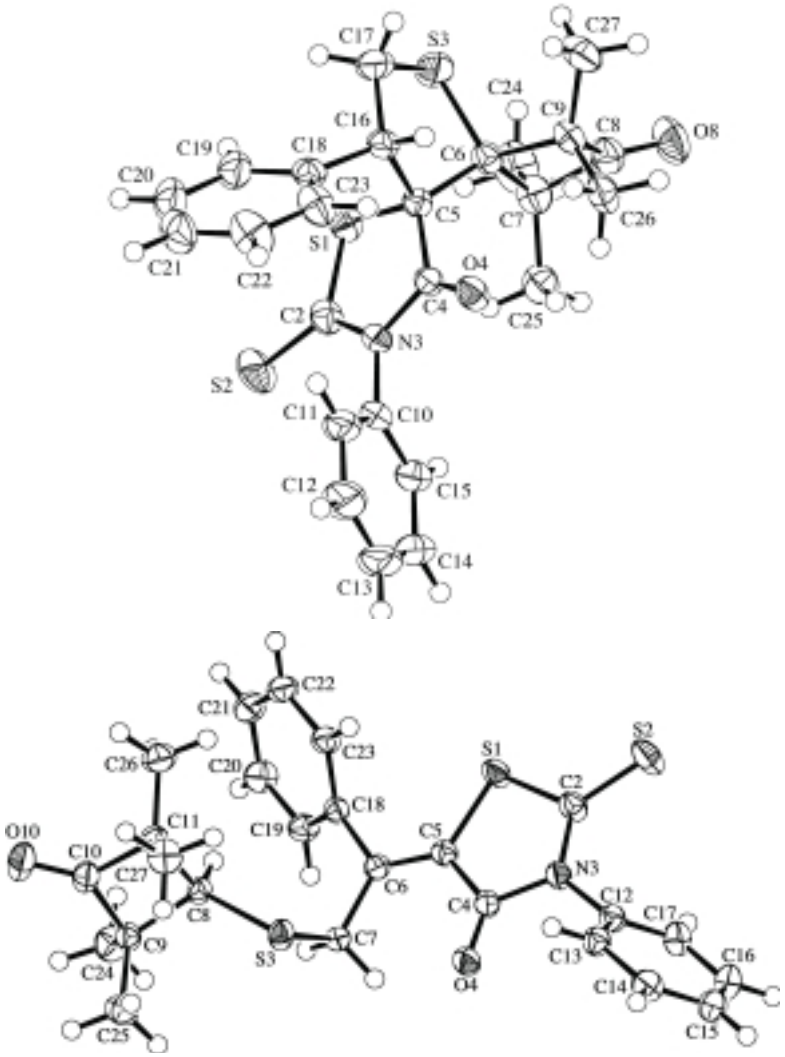
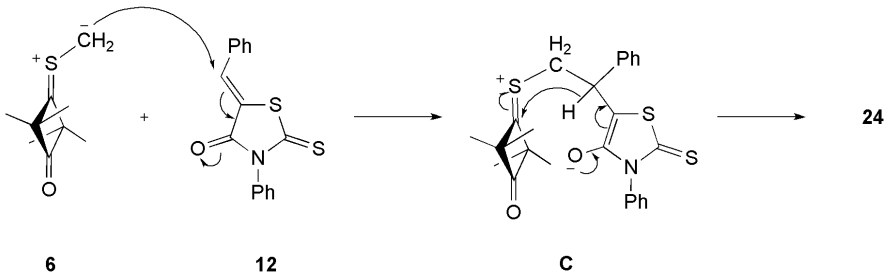


Figure 3. ORTEP-plots [29] of the molecular structures of one of the two symmetry-independent molecules of **23** (top) and of **24** (arbitrary numbering of the atoms; 50% probability ellipsoids).

The surprising structure of the second product, **24**, was again established by an X-ray crystal structure determination (Figure 3). A likely explanation for its formation is presented in Scheme 7 and is based on the assumption that the reaction with **6** may occur stepwise, in analogy to earlier described reactions of **6** with electron-deficient ethenes [13,33]. Addition of the nucleophilic thiocarbonyl ylide **6** to the exocyclic C,C-double bond of **12** in a Michael-type reaction could lead to the intermediate **C**, which gives the isolated products **23** and **24** *via* a 1,5-dipolar electrocyclization and a 1,4-H-shift, respectively.

Scheme 7



In conclusion, the experiments show that thiocarbonyl *S*-methanides **1a**, **6** and **20** react with **12** chemoselectively at the C,C-double bond to give spirocyclic tetrahydrothiophene derivatives. A 1,3-dithiolane as a minor adduct was observed only in the case of thiobenzophenone *S*-methylide (**1a**) and results from the addition occurring at the C=S group. This is a surprising result as, in general, C=S groups are known to be superior dipolarophiles, and benzonitrile oxide and -imides react with **12** at the C=S group exclusively. A possible explanation of the observed results is the high nucleophilicity of thiocarbonyl ylides and, therefore, a preference for nucleophilic addition onto the α,β-unsaturated ketone. In all examples, only one regioisomer, *i.e.* the sterically more crowded adduct was formed. Furthermore, the products consist of a single diastereoisomer as a racemate. The formation of **24** in the case of the sterically most congested thiocarbonyl *S*-methanide **6** is most likely a result of an H-shift in intermediate **C** (Scheme 7), which also could be the precursor of the cycloadduct **23** in a two-step reaction.

EXPERIMENTAL

1. General. See [16]. The ^{13}C-NMR spectra were recorded by using DEPT registration.

2. Starting materials. (*Z*)-5-Benzylidene-3-phenyl-2-thioxo-1,3-thiazolidin-4-one (benzylidenephenylrhodanine, **12**) was prepared in two steps following the protocol described in [28] (see also [26b]): treatment of 2-mercaptoacetic acid with phenyl isothiocyanate in a mixture of H_2O and EtOH gave *N*-phenylrhodanine in 77% yield. The latter reacted with benzaldehyde in refluxing acetic acid/sodium acetate to give **12** in 85% yield. Thiobenzophenone (**2**) [34,35], 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**3**) [36,37], and adamantanethione (**8**) [35,38] were synthesized according to known procedures.

3. Reaction of 12 with thiobenzophenone *S*-methylide (1a). A solution of **2** (0.612 g, 3.09 mmol) in CH_2Cl_2 (150 ml) under an argon atmosphere was cooled to –78°C, and 7.4 ml of a 0.5 M solution of diazomethane (*ca*. 3.7 mmol) in Et_2O were added, whereby the blue color of the solution disappeared. Then, a solution of **2** (0.918 g, 3.09 mmol) in CH_2Cl_2 was added and the solution was allowed to reach room temperature while stirring. After *ca*. 15 h, the solvent was evaporated and the residue was separated by column chromatography (SiO_2, hexane/ethyl acetate 5:1) to give **12** (0.271 g, 30%), **17** (0.964 g, 61%), and **18** (46 mg, 3%).

cis-*3,6,6,9-Tetraphenyl-2-thioxo-3-aza-1,7-dithiaspiro[4.4]nonan-4-one* (**17**): Colorless crystals, m.p. 264.0–264.5°C (CH_2Cl_2/hexane). R_f (hexane/ethyl acetate 5:1): 0.38. IR (KBr): 3057*w*, 2934v*w*, 1956v*w*, 1736v*s*, 1681*w*, 1593*w*, 1492*s*, 1454*m*, 1444*m*, 1343*s*, 1291*w*, 1243v*s*, 1180*m*, 1156*m*, 1072*m*, 1058*w*, 1032 *w*, 1003*w*, 779*w*, 766*w*, 740*s*, 698v*s*, 622*w*, 613*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.57–7.54

(*m*, 2 arom. H); 7.42–7.24 (*m*, 18 arom. H); 4.35 (*t*, *J* = 10.4, PhC*H*); 3.62 (*dd*-like, *J* = 8.2, 10.4, CH_2). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 198.9 (*s*, CS); 172.4 (*s*, CO); 142.7, 140.6, 135.0, 133.3 (4*s*, 4 arom. C); 130.5, 130.0, 129.4, 129.2, 129.0, 128.4, 128.3, 127.9, 127.6, 127.5, 127.1, 126.8 (12*d*, 20 arom. CH); 80.4, 74.2 (2*s*, spiro-C, Ph_2C); 55.9 (*d*, PhCH); 32.5 (*t*, CH_2). ESI-MS (CH_2Cl_2/MeCN 1:1 + NaI): 532 (100, $[M + Na]^+$). Anal. Calc. for $C_{30}H_{23}NOS_3$ (509.70): C 70.69, H 4.55, N 2.75, S 18.87. Found: C 70.64, H 4.54, N 2.70, S 18.86.

Suitable crystals for an X-ray crystal-structure determination were obtained by isothermal distillation of pentane into a solution of **17** in CH_2Cl_2/hexane.

(Z)-7-Benzylidene-4,4,9-triphenyl-9-aza-1,3,6-trithiaspiro[4.4.]nonan-8-one (**18**). Colorless solid, m.p. 211–212°C (CH_2Cl_2/hexane). R_f (hexane/ethyl acetate 5:1): 0.25. IR (KBr): 3056*w*, 2981v*w*, 2912v*w*, 1767*w*, 1684v*s*, 1608*w*, 1491*s*, 1444*m*, 1411*w*, 1332v*s*, 1286*w*, 1224*w*, 1189*s*, 1115*m*, 1078*w*, 1034*m*, 1019*m*, 918*w*, 884*w*, 825*w*, 785*w*, 761*w*, 749*w*, 719*s*, 695*s*, 642*w*, 607*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.63–7.20 (*m*, 20 arom. H, PhC*H*); 3.84, 3.59 (*AB*, *J* = 8.4, CH_2). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 166.8 (*s*, CO); 144.3, 139.6, 138.6, 134.6 (4*s*, 4 arom. C); 129.7, 129.5, 129.0, 128.8, 128.3, 127.4 (6*d*, 20 arom. CH, PhCH); 123.8 (*s*, PhCH=*C*); 93.4 (*s*, spiro-C); 76.3 (*s*, Ph_2C); 31.9 (*t*, SCH_2S). ESI-MS (MeOH + NaI): 532 (100, $[M + Na]^+$).

(Z)-5-Benzylidene-2-diphenylmethylene-3-phenyl-1,3-thiazolidin-4-one (**19**). A slightly acidic solution of **18** in $CDCl_3$ turned yellow and a solid precipitated. Filtration and evaporation of the solid gave **19** in quantitative yield.*

4. Reaction of 12 with adamantanethione *S*-methylide (20). A solution of **8** (0.165 g, 0.99 mmol) in toluene (50 ml) under an argon atmosphere was cooled to –20°C, and 2.6 ml of a 0.5 M solution of diazomethane (*ca*. 1.3 mmol) were added in two portions. After stirring for 2 h, the orange color of the solution vanished, and a solution of **12** (0.298 g, 1.00 mmol) in toluene (10 ml) was added. The mixture was heated to reflux (*ca*. 140°C) for 12 h, then the solvent was evaporated and the residue was separated by column chromatography (SiO_2, hexane/ethyl acetate 5:1) to yield **12** (0.206 g, 69%) and **21** (0.125 g, 28%).

Spiro[4-oxo-3,9-diphenyl-2-thioxo-3-aza-1,7-dithiaspiro[4.4]nonane-6,2'-tricyclo[3.3.1.1^{3,7}]decane] (**21**). Pale yellow crystals, m.p. 211–213°C (CH_2Cl_2/hexane). R_f (hexane/ethyl acetate 5:1): 0.55. IR (KBr): 3057*w*, 3031v*w*, 2937*m*, 2908v*s*, 2867*m*, 2851*s*, 1726v*s*, 1593*w*, 1493*m*, 1472*w*, 1453*m*, 1446*m*, 1340*s*, 1314*w*, 1291*w*, 1241v*s*, 1176*m*, 1166*m*, 1138*w*, 1098*m*, 1084*w*, 1072*w*, 1026*w*, 991*w*, 950*w*, 913*w*, 839*w*, 770*w*, 751*w*, 738*m*, 730*m*, 699*s*, 689*s*, 611*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.48–7.31 (*m*, 10 arom. H); 4.51 (*dd*, *J*(*trans*) = 11.7, *J*(*cis*) = 7.3, PhC*H*); 3.28–3.12 (*m*, CH_2); 2.75 (br. *s*, 1 H); 2.68–2.65 (*m*, 2 H); 2.48 (br. *d*, *J* = 13.9, 1 H); 2.14 (br. *d*, *J* = 13.0, 1 H); 1.95–1.59 (*m*, 9 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 199.0 (*s*, CS); 175.0 (*s*, CO); 135.2, 134.5 (2*s*, 2 arom. C); 130.3, 129.4, 129.3, 128.6, 128.1, 127.8 (6*d*, 10 arom. CH); 81.7, 73.9 (2*s*, 2 spiro-C); 58.3 (*d*, PhCH); 39.6 (*d*, adamantane CH); 38.0 (*t*, 2 adamantane CH_2); 37.4 (*d*, adamantane CH); 36.7, 35.8, 34.1, 31.7 (4*t*, 4 adamantane CH_2); 26.7, 25.9 (2*d*, 2 adamantane CH). ESI-MS (CH_2Cl_2/MeCN + NaI): 500 (100, $[M + Na]^+$). Anal. Calc. for $C_{27}H_{27}NOS_3$ (477.70): C 67.88, H 5.70, N 2.93, S 20.14. Found: C 67.98, H 5.62, N 2.84, S 20.15.

Suitable crystals for an X-ray crystal-structure determination of **21** were obtained by isothermal distillation of pentane into a solution of **21** in CH_2Cl_2/hexane.

5. Reaction of 12 with 2,2,4,4-tetramethyl-3-thioxocyclobutane *S*-methylide (6). A solution of **3** (0.628 g, 4.02 mmol) in Et_2O (10 ml) under an argon atmosphere was cooled to –78°C, and 15 ml of a 0.5 M solution of diazomethane (*ca*. 7.5 mmol) were added in two portions. The red color of the solution disappeared after stirring for 2 h. Then, the solvent was removed at 0°C by bubbling N_2 gas through the solution. The solid residue was dissolved with pentane (15 ml) at 0°C, the solution was cooled to –78°C, and the crystallized *1,1,3,3-tetramethyl-5-thia-7,8-diazaspiro[3.4]oct-7-en-2-one* (**22**) was isolated by decantation. Yield: 0.694 g (87%). A solution of **22** (0.596 g, 3.00 mmol) and **12** (0.638 g, 2.14 mmol) in THF (10 ml) under an argon atmosphere was heated to 50°C, when the evolution of N_2 started. After 2 h, the evolution of N_2 ceased (64 ml N_2, 2.9 mmol), the solvent was evaporated and the residue was separated by column chromatography (SiO_2, hexane/ethyl acetate 5:1) to give **12** (467 mg, 74%), **23** (81 mg, 8%), and **24** (104 mg, 10%).

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*The same product was obtained in 93% yield from **12** and diphenyldiazomethane in toluene [30].

1,1,3,3-Tetramethyl-8,10-diphenyl-7-thioxo-8-aza-6,12-dithiaspiro[3.0.4.3]dodecane-2,9-dione (**23**). Pale yellow crystals, m.p. 208–209°C. R_f (hexane/ethyl acetate 5:1): 0.34. IR (KBr): 3054v*w*, 2968*w*, 1783v*s*, 1738v*s*, 1680*m*, 1494*s*, 1471*m*, 1455*m*, 1417*m*, 1383*m*, 1352*s*, 1246v*s*, 1176*s*, 1135*m*, 1090*m*, 971*m*, 900*m*, 844*m*, 825*m*, 779*m*, 724*m*, 700*s*, 687*m*, 613*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.56–7.27 (*m*, 10 arom. H); 4.13 (*t*, *J* = 9.6, PhC*H*); 3.40–3.31 (*m*, CH_2); 1.82, 1.66, 1.65, 1.39 (4*s*, 4 Me). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 217.3 (*s*, CO); 199.2 (*s*, CS); 172.5 (*s*, CO); 135.2, 133.7 (2*s*, 2 arom. C); 129.7, 129.5, 129.3, 129.1, 128.9, 128.5, 128.3, 127.6 (8*d*, 10 arom. CH); 82.5, 74.3 (2*s*, 2 spiro-C); 69.7, 62.7 (2*s*, 2 Me_2C); 57.81 (*d*, PhCH); 32.1 (*t*, CH_2); 25.7, 24.3, 22.5, 22.1 (4*q*, 4 Me). ESI-MS ($MeCN/CH_2Cl_2$ 1:1 + NaI): 490 (100, $[M + Na]^+$). Anal. Calc. for $C_{25}H_{25}NO_2S_3$ (467.67): C 64.21, H 5.39, N 3.00, S 20.57. Found: C 64.02, H 5.36, N 2.87, S 20.50.

Suitable crystals for an X-ray crystal-structure determination were obtained by isothermal distillation of pentane into a solution of **23** in 1,2-dimethoxyethane.

3-Phenyl-5-{1-phenyl-2-[(2',2',4',4'-tetramethylcyclobutan-1'-yl)thio]ethylidene}-2-thioxo-1,3-thiazolidine-3',4-dione (**24**): Orange crystals, m.p. 154–158°C. R_f (hexane/ethyl acetate 5:1): 0.31. IR (KBr): 3045v*w*, 2959*m*, 2923*w*, 2861*w*, 1770v*s*, 1710v*s*, 1590*m*, 1569*w*, 1491*m*, 1456*m*, 1441*w*, 1415*w*, 1379*w*, 1364*w*, 1347*s*, 1315*w*, 1291*w*, 1247v*s*, 1183*s*, 1157*m*, 1092*w*, 1073*w*, 1024*m*, 914*w*, 841*w*, 764*w*, 729*m*, 700*m*, 689*m*, 639*w*, 630*w*, 612*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.58–7.43 (*m*, 7 arom. H); 7.38 (br. *s*, 1 arom. H); 7.26–7.23 (*m*, 2 arom. H); 4.38 (*s*, CH_2); 3.09 (*s*, CHS); 1.15, 1.14 (2*s*, 4 Me). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 219.9 (*s*, CO); 193.5 (*s*, CS); 165.4 (*s*, CO); 149.4 (*s*, PhC=*C*); 139.6, 134.9 (2*s*, 2 arom. C); 130.1, 129.6, 129.5, 129.2, 128.3, 128.0, 127.2 (7*d*, 10 arom. CH); 125.3 (*s*, Ph*C*=C); 60.3 (*s*, 2 Me_2C); 55.6 (*d*, CHS); 34.3 (*t*, CH_2); 24.4, 19.8 (2*q*, 4 Me). ESI-MS (CH_2Cl_2 + NaI): 490 (100, $[M + Na]^+$), 468 (18), 420 (31), 333 (9), 304 (16).

Suitable crystals for an X-ray crystal-structure determination of **24** were obtained by isothermal distillation of pentane into a solution of **24** in $CDCl_3$/hexane.

6. X-ray crystal-structure determination of 17, 21, 23 and 24 (see Table 1 and Figs. 1–3)*). All measurements were made on a Nonius KappaCCD diffractometer [39] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [40]. The intensities were corrected for Lorentz and polarization effects, and absorption corrections based on the multi-scan method [41] were applied. Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1, and views of the molecules are shown in Figs. 1–3. The structures of **17**, **21** and **23** were solved by direct methods using SIR92 [42], which revealed the positions of all non-H-atoms. In the case of **23**, there are two symmetry-independent molecules in the asymmetric unit. The coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program PLATON [43], but none could be found. The structure of **24** was solved by heavy-atom Patterson methods [44], which revealed the positions of the S-atoms. All remaining non-H-atoms were located in a Fourier expansion of the Patterson solution, which was performed by DIRDIF94 [45]. For each structure, the non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups of **23** and **24**). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied for **23**. In the cases of **17**, **21** and **23**, three, two and eight reflections, respectively, whose intensities were considered to be extreme outliers, were omitted from the final refinement. For **23**, the largest peak of residual electron density was 2.36 Å from atom H(15), but could not be rationalised with a chemically logical position, nor could it be refined successfully as a partial occupancy water molecule. Neutral atom scattering factors for non-H-atoms were taken from [46a], and the scattering factors for H-atoms were taken from [47]. Anomalous dispersion effects were included in F_c [48]; the values for *f*' and *f*" were those of [46b]. The values of the mass attenuation coefficients are those of [46c]. All calculations were performed using the SHELXL97 [49] program.

*CCDC-294731–294734 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for compounds **17**, **21**, **23** and **24**.

	17	**21**
Crystallized from	CH_2Cl_2/hexane/pentane	CH_2Cl_2/hexane/pentane
Empirical formula	$C_{30}H_{23}NOS_3$	$C_{27}H_{27}NOS_3$
Formula weight [g mol^{-1}]	509.70	477.70
Crystal color, habit	colorless, prism	pale yellow, prism
Crystal dimensions [mm]	0.15 × 0.20 × 0.25	0.17 × 0.20 × 0.30
Temperature [K]	160(1)	160(1)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Z	2	4
Reflections for cell determination	46235	34682
2θ range for cell determination [°]	4 –60	4–60
Unit cell parameters a [Å]	10.3260(2)	12.7901(2)
b [Å]	11.2042(2)	10.9689(2)
c [Å]	11.3691(1)	16.3241(2)
α [°]	98.8038(9)	90
β [°]	92.4303(9)	101.2457(8)
γ [°]	107.7516(7)	90
V [Å^3]	1232.40(3)	2246.19(6)
D_X [g cm^{-3}]	1.373	1.412
μ(Mo$K\alpha$) [mm^{-1}]	0.326	0.352
Scan type	φ and ω	φ and ω
2θ (max) [°]	60	60
Transmission factors (min; max)	0.871; 0.955	0.864; 0.942
Total reflections measured	36407	60592
Symmetry independent reflections	7170	6570
Reflections with $I > 2\sigma(I)$	5809	5505
Reflections used in refinement	7167	6568
Parameters refined	316	289
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0386	0.0348
$wR(F^2)$ (all data)	0.1034	0.0923
Weights:[a] a; b	0.05; 0.509	0.0441; 0.9598
Goodness of fit	1.024	1.053
Secondary extinction coefficient	–	–
Final Δmax/σ	0.001	0.001
Δρ (max; min) [e Å^{-3}]	0.34; –0.37	0.35; –0.36

[a] $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$

Table 1. Crystallographic data for compounds **17**, **21**, **23** and **24** (continued).

		23	**24**
Crystallized from		DMOE/pentane	$CDCl_3$/hexane/pentane
Empirical formula		$C_{25}H_{25}NO_2S_3$	$C_{25}H_{25}NO_2S_3$
Formula weight [g mol^{-1}]		467.66	467.66
Crystal color, habit		pale yellow, prism	orange, prism
Crystal dimensions [mm]		0.20 × 0.25 × 0.28	0.22 × 0.25 × 0.28
Temperature [K]		160(1)	160(1)
Crystal system		triclinic	triclinic
Space group		$P\bar{1}$	$P\bar{1}$
Z		4	2
Reflections for cell determination		207466	55709
2θ range for cell determination [°]		4 –55	4–60
Unit cell parameters	a [Å]	8.4135(2)	8.0529(2)
	b [Å]	15.7231(4)	11.4487(2)
	c [Å]	19.1282(5)	13.2158(2)
	α [°]	111.005(1)	79.4247(9)
	β [°]	90.423(2)	85.547(1)
	γ [°]	94.551(2)	78.1303(8)
	V [Å^3]	2353.1(1)	1171.12(4)
D_X [g cm^{-3}]		1.320	1.326
μ(Mo$K\alpha$) [mm^{-1}]		0.337	0.339
Scan type		φ and ω	ω
2θ (max) [°]		55	60
Transmission factors (min; max)		0.798; 0.972	0.833; 0.931
Total reflections measured		56591	47462
Symmetry independent reflections		10476	6849
Reflections with $I > 2\sigma(I)$		7818	5150
Reflections used in refinement		10468	6849
Parameters refined		568	284
Final $R(F)$ [$I > 2\sigma(I)$ reflections]		0.0567	0.0416
$wR(F^2)$ (all data)		0.1577	0.1135
Weights:[a] a; b		0.0762; 2.0292	0.0552; 0.371
Goodness of fit		1.034	1.040
Secondary extinction coefficient		0.005(1)	–
Final Δ_{max}/σ		0.001	0.001
Δρ (max; min) [e Å^{-3}]		1.42; –0.57	0.31; –0.40

[a] $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$

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